

HEAT TREATMENT OF COALS IN HYDROGEN-DONATING SOLVENTS
AT TEMPERATURES AS LOW AS 175-300°C

Masashi Iino and Jianli Shen
Institute for Chemical Reaction Science, Tohoku University,
Katahira 2-1-1, Aoba-ku, Sendai 980, Japan

Keywords; Heat treatment, Bituminous coal, Hydrogen-donating solvent

INTRODUCTION

CS₂-N-methyl-2-pyrrolidinone (NMP) mixed solvent (1:1 by volume) gave high extraction yields (40-65%, daf) at room temperature for many bituminous coals (1). We also found that the extracts obtained include a considerable amount of the very heavy extract component which is not soluble in THF or pyridine, but soluble in the mixed solvent (2). This mixed solvent was used as an extraction solvent for the heat treatment products of the bituminous coals at 300-450°C in tetralin (TET) or naphthalene (NAP) (3). The results showed that retrogressive reactions occur more readily for the heaviest fraction, i.e., THF-insoluble, CS₂-NMP mixed solvent soluble fraction (TIMS) than other lighter fractions such as benzene-insoluble, THF-soluble (preasphaltene). The heat treatment of TIMS itself, which was obtained from the extraction of Zao Zhuang coal with the CS₂-NMP mixed solvent at room temperature, in several solvents at 100-350°C showed that retrogressive reaction, i.e., the conversion of TIMS to the mixed solvent insoluble fraction (MI), was suppressed by adding a strong hydrogen-donating solvent such as 9,10-dihydroanthracene (DHA) or 1,4,5,8,9,10-hexahydroanthracene (HHA) (4). It was also found that as more hydrogen was transferred from the solvent to TIMS, the extent of the retrogressive reaction decreased.

In this study, heat treatments of raw Zao Zhuang and Upper Freeport coals were carried out at 175-300°C in various solvents. The coal was found to undergo either retrogressive or dissolution reaction even at temperatures as low as 175°C, depending on the hydrogen donatability of the solvent used. The mechanisms for these reactions are discussed.

EXPERIMENTAL

Zao Zhuang (China) and Upper Freeport (Argonne Premium Coal, USA) coals were used. The ultimate and proximate analyses are given in Table 1. Heat treatment solvents used are TET, NAP, 1-methylnaphthalene (MNA), DHA, HHA and liquefaction recycle solvent (LRS). LRS (88.5%C, 9.7%H) was obtained from the 1t/day liquefaction plant of Wyoming coal operated by NEDO (New Energy Development Organization, Japan).

Heat treatment of the coal was performed in 50mL magnetically stirred autoclave at 175, 250, and 300°C, respectively. 1g of the coal and 5g of the solvent were charged to the autoclave, which was pressurized with nitrogen to 5.0 MPa at room temperature. After the heat treatment, the coal components were fractionated into the CS₂-NMP mixed solvent-insoluble fraction (MI) and -soluble fraction (MS), and then MS further into TIMS and TS (and the solvent), with the mixed solvent and THF at room temperature under ultrasonic irradiation, as shown in Figure 1. The quantity of MI and TIMS was determined after drying overnight in vacuum oven at 80°C and that of TS was calculated by difference, i.e., 100-MI-TIMS. The dissolution yield was defined here as the sum of TIMS and TS.

The quantity of hydrogen transferred from DHA and HHA to the coal was determined from GC analysis. GC showed that the main solvent-derived products are anthracene for the heat treatment in DHA, and tetrahydroanthracene and octahydroanthracene for

that in HHA, respectively. Hydrogen transferred in both treatments was determined from the quantity of anthracene, and from the difference of tetrahydroanthracene and octahydroanthracene, respectively.

RESULTS

Figure 2 shows the fraction distribution after the heat treatment of Zao Zhuang coal in 5 solvents at 175°C, 250°C and 300°C, together with that for the raw coal, which was obtained from the fractionation of the extract of the raw coal with the CS₂-NMP mixed solvent at room temperature. At 175°C and 250°C in NAP and TET, MI increased and TMS decreased, compared with those for the raw coal. While, in a strong hydrogen-donating solvent such as DHA and HHA, MI decreased and TS increased by the treatment. Contrary to the results at 175°C and 250°C, MI decreased and TS increased in TET at 300°C. The same tendency was observed, to a lesser extent in NAP, than TET. In DHA, HHA and LRS the decrease of MI and the increase of TS was further enhanced at 300°C. Especially, in HHA, TS increased to 42.1% from 13.8% of the raw coal and the dissolution yield, i.e., TMS + TS increased to 83.4% from 63.0% of the raw coal. The dissolution yield and TS are the order of HHA > DHA > LRS. Figure 3 shows that Upper Freeport coal gave similar results as those for Zao Zhuang coal, except that MI did not decrease at 300°C with MNA or TET, and the dissolution yields are 86.8% and 90.6% at 300°C in DHA and HHA, respectively, which are higher than that for Zao Zhuang coal.

Figure 4 shows the dependence of the fraction distribution on the heat treatment time for Zao Zhuang coal in HHA at 250°C. The Figure shows that for the reaction times up to 1 h MI decreases and TS increases with increasing reaction time, but little change occurs over 1 h. Figure 5 and 6 show the dependence of hydrogen transferred from the solvent to the coal and the dissolution yield on the heat treatment temperature. The Figures indicate that the increase of the dissolution yield is closely related to the hydrogen transferred, and hydrogen transferred are always higher for HHA than those for DHA, indicating that HHA is a stronger hydrogen donating solvent than DHA. Figure 7 also shows that hydrogen transferred is well correlated with the dissolution yield when the heat treatment time was varied. Table 2 shows that spin concentration of acetone-insoluble fraction(AI) after the heat treatment of ZZ coal in HHA is much smaller than that of the raw ZZ coal. The yields(raw coal base) were more than 90% and acetone-soluble fraction has much smaller spin density than AI.

DISCUSSION

The result that MI increased and TMS decrease at 175°C and 250°C in TET indicates the occurrence of retrogressive reactions. Although TET is often used as a hydrogen-donating solvent in the study of coal liquefaction above 350°C, this result indicates that TET was little hydrogen-donating like NAP or MNA at the low temperatures. While, in a much stronger hydrogen-donating solvent than TET, i.e., DHA or HHA, the hydrogen donation from the solvent to the coal occurs even at 175°C and 250°C, resulting in the dissolution reactions, i.e., the decrease of MI and the increase of TS. These dissolution reactions occur more easily at 300°C.

When temperature rises to 300°C, the hydrogen donatability of TET and the reactivity of the coal radicals may increase. So, the retrogressive reaction in TET was suppressed. NAP, which has no donatable hydrogens, gave no suppression of the retrogressive reaction even at 300°C. MNA also gave a similar result as NAP. It should be noticed that LRS is a better solvent than TET in this treatment. It is probably due to the fact that LRS

contains a lot of hydrogenated condensed aromatic compounds which can easily donate hydrogens.

The close relationship between the dissolution yield and the quantity of hydrogen transferred from the solvent to the coal and the decrease of radical concentration after the heat treatment indicated that coal radicals may be responsible for the results observed here. When the radicals are stabilized by the hydrogen donation, the dissolution occurs. While, in a poor hydrogen donating solvent which hardly donate hydrogen to the radicals, retrogressive reactions such as the addition to aromatic rings of coal network and coupling reactions between them may occur. It is not clear that the radicals, which are responsible for the dissolution and retrogressive reaction, are formed by the scission of weak covalent bonds and/or indigenous radicals activated by heat at 175-300°C. The fact that the extent of the dissolution reaction increased with the heat treatment time up to 1 h suggests that the dissolution reactions are rather slow. So, the radicals may be formed by slow bond scissions, not indigenous ones, since the thermal activation of the latter radicals seems to be a rapid process. There are several kinds of weak covalent bonds which break at these low temperatures. For example, it is well known that as the number of phenyl groups replacing hydrogen atoms in ethane increases, its central C-C bond strength markedly decreases, and pentaphenylethane readily dissociates into the triphenylmethyl and diphenylmethyl radicals below 100°C. Stronger bonds than described above are possibly broken by solvent-mediated hydrogenolysis proposed by Malhotra and McMillen(5).

Finally, it should be noted that the results above described were obtained by the use of the CS₂-NMP mixed solvent as an extraction solvent for the reaction mixture. If THF is used as an extraction solvent instead of the mixed solvent, we can only see small change of TS by the heat treatments carried out here.

CONCLUSIONS

Heat treatments of Zao Zhuang and Upper Freeport coals were carried out in several hydrogen-donating solvents at 175-300°C under N₂ atmosphere. Retrogressive reaction of the coal was observed in TET at temperatures as low as 175-250°C. While, in DHA or HHA, which are much stronger hydrogen donors than TET, the coal underwent dissolution reactions at 175-300°C. The quantity of hydrogen transferred from the solvents to coals was found to be well correlated with the degree of the dissolution reactions, and spin concentration in coal components decreased after the dissolution reactions, suggesting hydrogen donation to coal radicals in this heat treatment.

ACKNOWLEDGEMENT

The authors thank NEDO(New Energy and Development Organization, Japan) for providing LRS sample used in this research. This work was supported by a Grant-in Aid for Energy Research from Ministry of Education, Science and Culture, Japan.

REFERENCES

- (1) Iino, M.; Takanohashi, T.; Ohsuga, H.; Toda, K. *Fuel* 1988, 67, 1639-1647.
- (2) Iino, M.; Takanohashi, T.; Obara, S.; Tsueta, H.; Sanokawa, Y. *Fuel* 1989, 68, 1588-1593.
- (3) Wei, X.; Shen, J.; Takanohashi, T.; Iino, M. *Energy Fuels* 1989, 3, 575-579.
- (4) Shen, J.; Takanohashi, T.; Iino, M. *Energy Fuels* 1992, 6, 854-858.
- (5) Malhotra, R.; McMillen, D.F. *Energy Fuels* 1993, 7, 227-233.

Table 1 Ultimate and Proximate analyses of the coals

	Ultimate analysis (wt%, daf)					Proximate analysis (wt%, db)		
	C	H	N	S	O*	VM	Ash	FC
Zao Zhuang	86.9	5.1	1.5	1.6	4.9	28.6	7.4	64.0
Upper Freeport	86.2	5.1	1.9	2.2	4.6	28.2	13.1	58.7

*By difference

Table 2 Spin Concentration of Zao Zhuang coal and acetone-insoluble fraction (AI) of coal components after the heat treatment in HHA

	heat treatment (HHA, 1 h)	yield ^a (wt %, db)	spin concentration (10 ¹⁰ spin/g, daf)
raw coal	-	-	2.34
AI	175 °C	96.3	2.04
AI	250 °C	94.4	1.68
AI	300 °C	89.8	0.91

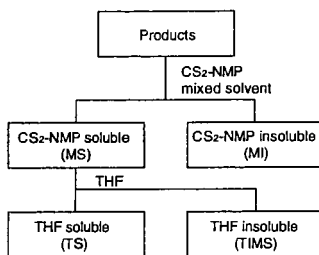
^aBased on the raw coal

Figure 1 Extraction and fractionation procedures for the heat treatment mixture.

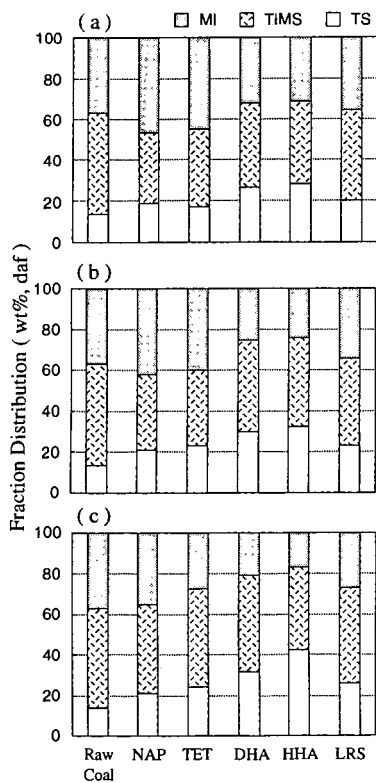


Figure 2 Fraction distribution after the heat treatment of Zao Zhuang coal in NAP, TET, DHA, HHA and LRS at 175°C (a), 250°C (b) and 300°C (c) for 1h, together with that for the raw coal.

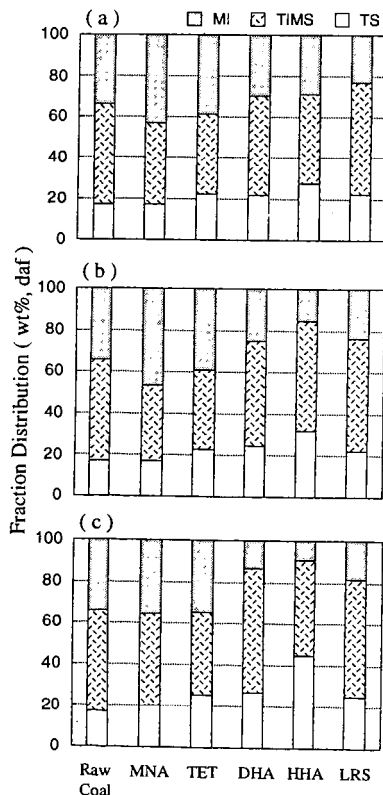


Figure 3 Fraction distribution after the heat treatment of Upper Freeport coal in MNA, TET, DHA, HHA and LRS at 175°C (a), 250°C (b) and 300°C (c) for 1h, together with that for raw coal.

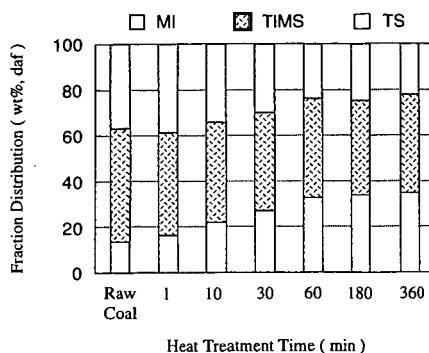


Figure 4 Fraction distribution after the heat treatment of Zao Zhuang coal in HHA at 250°C for 1-360 min, together with that for the raw coal.

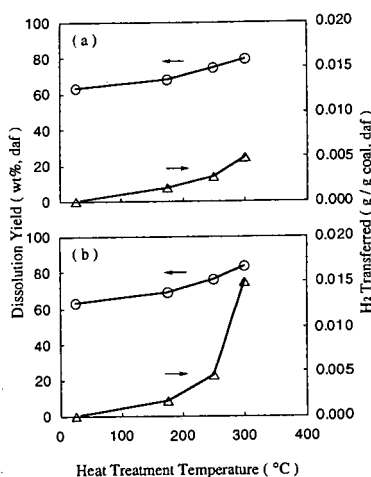


Figure 5 Plots of dissolution yield(\circ) and H_2 transferred(Δ) with heat treatment temperature for Zao Zhuang coal in DHA(a) and HHA(b) for 1h.

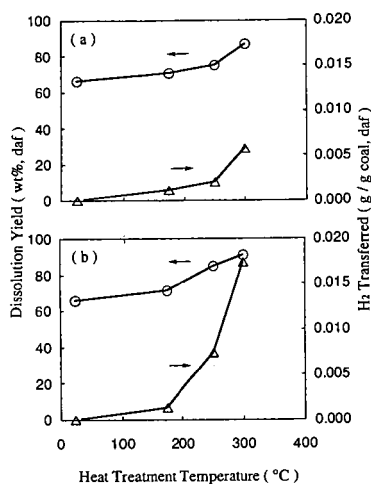


Figure 6 Plots of dissolution yield(\circ) and H_2 transferred(Δ) with heat treatment temperature for Upper Freeport coal in DHA(a) and HHA(b) for 1h.

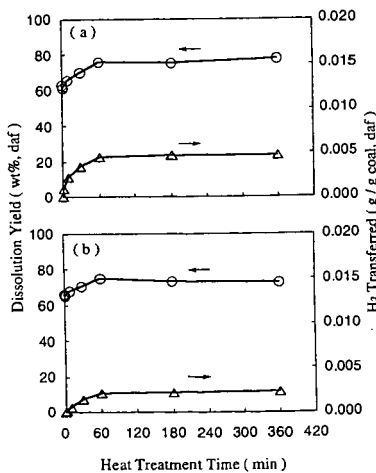


Figure 7 Plots of dissolution yield(\circ) and H_2 transferred(Δ) with heat treatment time for Zao Zhuang coal in HHA(a) and Upper Freeport coal in DHA(b) at 250°C.